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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C01B 15/055

A1

(11) International Publication Number: WO 96/09983

(43) International Publication Date: 4 April 1996 (04.04.96)

(21) International Application Number: PCT/US95/12427

(22) International Filing Date: 26 September 1995 (26.09.95)

(30) Priority Data:
08/312,000 26 September 1994 (26.09.94) US

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(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: STABLE PERACID SOLS, GELS AND SOLIDS AND A PROCESS THEREFOR

(57) Abstract

A stable composition is provided of an aqueous peroxycarboxylic acid sol or gel and a cross-linked polyacrylate with a pH greater than 3.5. A process for preparing the composition is also disclosed.

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STABLE PERACID SOLS, GELS AND SOLIDS AND A PROCESS THEREFOR

The present invention is a process to form a stable aqueous polyacrylate sol or gel containing a peracid.

Environmental concerns about the effects of certain chemicals on the upper atmosphere has led to some unease about the widespread use of chlorine bleach. Hydrogen peroxide, peracetic acid, persulfates and peroxyhydrates, such as sodium perborate are well known as alternative bleaching compounds to available chlorine compounds but have not been found suitable to replace liquid chlorine bleach.

Hydrogen peroxide would be ideal because its end-products are only water and oxygen. However, to act as a bleach it is necessary to increase the pH of the solution to at least 7 or 8; where the hydrogen peroxide solution is not storage stable. Peracetic acid, even at a lower pH, is an even more powerful oxidizing agent than hydrogen peroxide, but it is difficult to handle because of its strong odor and because it can cause chemical "burns" if splashed onto the skin. The persulfates and inorganic peroxyhydrates generally contribute large amounts of undesired dissolved solids to the effluent when they are employed.

It is particularly desirable that a liquid bleach be available for use as a single, stable viscous solution (sol) or a gel, although a solid would be satisfactory if it were biodegradable, easily soluble in water, and did not contain significant inorganic dissolved solids such as are provided by sodium persulfate or sodium perborate.

Highly viscous hydrogen peroxide sols are well known. U.S. Patent 959,605 to Queisser (1910) discloses that

vegetable gums were well known at that time to be useful for thickening and gelling hydrogen peroxide. The patent also teaches incorporating burnt gypsum which by hydrating further stabilizes the hydrogen peroxide and the hydrated gypsum is useful as an abrasive. U.S. Patent 3,658,712 to Lindner (1972) claims a stable thickened aqueous suspension of sodium perborate of polymers containing carboxyl groups, preferably a poly-carbonate polymethacrylate. The specific polymer, Carbopol 934, was cited as the thickening agent. U.S. Patent 5,102,571 to Mole et al. (1992) teaches an aqueous solution or suspension of sodium perborate tetrahydrate thickened to form a mobile fluid, or a high viscosity paste or gel. The thickening agents disclosed were a hydroxyalkyl cellulose, polysaccharides (that is, xanthan and galactomannan gums), fumed silica and clays, plus a dispersing agent such as a sodium salt of polyacrylic acid. In addition to the above, there are two patents claiming stable, thickened hydrogen peroxide sols, U.S. Patents 3,499,844 and 4,130,501 which employ polyacrylics (the latter with an added surfactant). However, to be useful as a bleach these sols require further compounding to increase the pH to at least 8, or must be packaged in an expensive two-compartment package. On the other hand, thickened perhydrate suspension, such as the sodium perborate composition of U.S. Patent 3,658,712 contributes undesirable non-biodegradable dissolved solids to the environment, including phytotoxic borate ions.

Other prior attempts to provide a peroxygen-based bleach have included gelled suspensions of substantially insoluble peracids, such as diperazelic acid (U.S. Patent 3,996,152). The patent discloses that the water-insoluble peracids require salt-forming alkaline conditions to provide a solution of the active oxygen

bleaching species. In general peracids themselves are effective bleaching agents even at a low pH, provided they are solubilized.

U.S. Patent 4,879,057 attempts to overcome some of the disadvantages of the product of U.S. Patent 3,996,152 by providing pourable to pasty aqueous bleaching agent suspensions which have practically no solid/liquid phase separation and only a slight loss of available oxygen, even after two weeks of storage. The patent teaches a composition comprising an aqueous carrier liquid, a particulate, practically water-insoluble peroxycarboxylic acid, an organic thickening agent (starch) and an acidifying agent, which is characterized in that it contains a xanthan polysaccharide or agar polysaccharide as thickening agent and a hydrate-forming neutral salt which desensitizes peroxycarboxylic acids, such as sodium sulfate, sodium phosphate, sodium borate or the like. The bleaching agent still requires the alkaline conditions, provided by a laundry detergent to dissolve the peracid sufficiently to provide bleaching conditions.

The present invention overcomes the problems of the prior art by providing an aqueous colloidal peracid composition comprising stable sols, gels and solids of C2 to C6 peroxycarboxylic acids and a cross-linked polyacrylate. Optionally the composition may further comprise conventional additives and gel-assisting agents for a polyacrylate. The invention is also a process for forming a stable aqueous peroxycarboxylic gel by incorporating a cross-linked polyacrylate thereof into an aqueous solution to form an aqueous sol, incorporating therein a peroxycarboxylic acid and subsequently adjusting the pH to 3 or above.

The aqueous solution may be water or an aqueous solution of hydrogen peroxide. The pH may be adjusted

by adding an inorganic alkaline material, such as sodium hydroxide, potassium hydroxide, sodium carbonate, magnesium hydroxide or the like to the aqueous peroxycarboxylate sol, provided the alkaline material is not a peroxygen decomposition catalyst.

Another important component is that of the cross-linked polyacrylic polymer. The polyacrylic polymer should be one that is interpolymerized with a multi-vinyl or multi-allylic functionalized cross-linking agent. Preferably, the polyacrylic polymer is interpolymerized with a polyalkenyl polyether of a polyhydric compound. The polyhydric compound should have at least 4 carbons and 3 hydroxy groups. These thickeners are described in U.S. Pat. No. 2,798,053 and U.S. Pat. No. 4,130,501, both of which are herein incorporated by reference. More specifically the thickeners are water dispersible copolymers of an alpha-beta monoolefinically unsaturated lower aliphatic acrylic acid cross-linked With a polyether of a polyol. The polyol may be selected from the group consisting of oligosaccharides, reduced derivatives thereof in which the carbonyl group is converted to an alcohol group, and pentaerythritol. The hydroxy groups of said polyol are etherified with allyl groups, said polyol having at least two allyl groups per polyol molecule. A suitable copolymer is one of acrylic acid with low percentages (0.71 to 1.5%) poly ally sucrose.

Molecular weights of the cross-linked polymer may range from about 500,000 up to 10,000,000, and preferably between 600,000 and 2,000,000. Examples of commercially available cross-linked polymers based upon allyl sucrose modified polyacrylic acid are the Carbopol Registered TM resins manufactured by the B.F. Goodrich Chemical Company. These materials include Carbopol 941 Registered TM (m.w. 1,250,000), Carbopol 934 Registered

TM (m.w. 3,000,000) and Carbopol 940 Registered TM (m.w. 4,000,000). The optimal choice will depend on the desired and clarity and can be easily selected by consulting the manufacturers data sheets and a few simple experiments.

The polyacrylic polymer of this invention may be present in an amount from about 0.1 to about 10%, preferably from about 0.5 to 2%, optimally between about 0.7 and 1.5% by weight of the composition depending upon the desired viscosity and the polyacrylic polymer selected.

The compositions are useful for delivering peracids and salts at a pH of 3.5 to 11 in applications such as surface cleaners, detergent bleach, automatic dish washing formulations and other cleaning applications. The compositions are particularly useful for sanitizing or bleaching at an acid or neutral pH compared with other chlorine or peroxygen bleach compounds.

It was unexpected from the prior art that thickened sols, gels or solids could be made from a water-soluble peroxycarboxylic acid (peracid) such as peracetic acid. Indeed, initial experiments were unsuccessful! It was particularly unexpected that storage stable thickened peracetic acid compositions could be prepared because such peracids are very strong oxidizing agents even at a pH of 2 to 8, unlike hydrogen peroxide which is usually a reducing agent in that pH range, and because the water soluble peracids are far less stable than hydrogen peroxide, decomposing to form free radicals which tend to depolymerize large molecules such as polyacrylates and hydrolyze esters. Heretofore, stable gels or sols have been made containing hydrogen peroxide but none are reported containing a water-soluble peracid. There is no suggestion in the prior art that a solid peracid composition could be prepared.

It is well known that aqueous peracids are an equilibrium composition. For peracetic acids the equilibrium is represented as follows:

$$CH_3COOH + H_2O_2 \longleftrightarrow CH_3COOOH + H_2O$$

The rate of the equilibrium reaction is very slow unless in the presence of a catalyst, such as a strong acid. Usually it is sufficient for a stability determination to determine only the total active oxygen of the compositions. It is, of course, preferable for some purposes to know the concentration of the peracid as well as the total active oxygen concentration.

Contrary to the teaching of U.S. Patents 3,499,844 and 4,130,501 it was found that a homogeneous sol or gel could not be formed by directly combining an aqueous peroxycarboxylic acid with a polyacrylate. Instead it is necessary initially to form an aqueous sol or gel by forming a mixture of water or aqueous hydrogen peroxide with the polyacrylate, and incorporating the peroxycarboxylic acid into the mixture as the viscosity increases. It is particularly desirable to incorporate hydrogen peroxide into the composition to favor a higher equilibrium concentration of peroxycarboxylic acid or salt. It is preferred to form the initial mixture by combining aqueous hydrogen peroxide with the polyacrylate.

Generally, adjusting the pH of the composition after adding the peroxycarboxylic acid has an adverse effect on the final viscosity of the composition. It is desirable that sufficient alkali be incorporated into the aqueous solution prior to adding the peroxycarboxylic acid.

It was most unexpected to find that the sols or gels were stable at a pH greater than 7 in view of the known instability of both hydrogen peroxide and peracid at a pH greater than 7.

For the purpose of this invention a "stable" sol, gel or solid peracid composition is one which maintains sufficient physical properties (viscosity) and active oxygen content long enough to be useful, at least 24 hours. To be "storage stable" the sol, gel or solid peracid composition should maintain at least 90% of its viscosity and active oxygen content for one month.

Any C2 to C6 percarboxylic acid which is water soluble may be incorporated into the compositions. Examples include peracetic acid, perproprionic acid, perbutyric acid, pervaleric acid, and percaproic acid.

Cross-linked polyacrylates are available in a range of molecular weights and can be derivatized (such as methacrylate). Polyacrylates are widely available under different tradenames (for example, CARBOPOL - Trademark of U.S. Goodrich Corp.).

Having described the best mode of practicing the invention the following examples are provided to illustrate the invention and not as a limitation thereof.

EXAMPLES

All the preparations were made under normal ambient laboratory conditions, approximately 1 atmosphere pressure and room temperature (17°C to 25°C). Vacuum drying when employed was at 40°C and from 3.5 to 10 kPa absolute. However, it is well known that some peracids, particularly peracetic acid, are more volatile than the corresponding acid or hydrogen peroxide. Therefore, it is necessary to ensure that vacuum drying be closely monitored to avoid extracting substantial amounts of the peracid also.

Formulations of peracids were prepared by adding the peracid to an aqueous sol which was in the process of thickening. Typically, the aqueous sol was prepared by adjusting 120 g of 5.0% (wt.) H2O2pH of about 9.5 with

50 wt. % sodium hydroxide or pellets and adding 0.61 g Carbopol 617 with vigorous stirring. If necessary, the pH was adjusted to pH 9.5 - 9.6 before the peracid was added. Polyacrylic formulations were prepared in the 1% to 6% range.

Unless otherwise indicated all proportions are by weight.

COMPARATIVE EXAMPLE A

Solid Carbopol 941 was added to 5% commercial peracetic acid with vigorous stirring. The Carbopol balled up and would not form a homogeneous sol.

EXAMPLE 1

A Peracetic Acid/Carbopol 941 Gel was formed by mixing the components and adjusting the pH to approximately 6.00 with dilute sodium hydroxide. A thickened solution containing 4.45% peracetic acid was obtained. This gel is stable at ambient conditions.

Carbopol 623, 1610, and 940 can be substituted for 941 to produce gel of similar viscosity and peracetic acid content. However, the best gel was made using Carbopol 934. Peracetic acid concentrations up to 9.78 can be obtained using 15% peracetic acid. No pH adjustment was needed to form the gel.

EXAMPLE 2

A gel was prepared at pH 5.1 containing 2% Carbopol 617 and 1% PAA. Initial assay was 1.69% H2O2 1.09% PAA. After 3 weeks the gel assayed 1.62% H2O2.65% PAA and had a pH of 4.5.

EXAMPLE 3

Commercial 5% peracetic acid (PAA) (or 15% for Examples 3C and 3D) was formulated into a series of polyacrylate gels containing about 1% PAA and 1% to 6% H2O2 typically as follows:

20 g 3% H2O2 and 20 g deionized water were adjusted to pH 9-10 with NaOH and about 0.5 g (1% by weight) polyacrylate was added (Carbopol 617) followed by 10 g of 5% PAA to form the peracetic acid gel. Samples were assayed initially and after 1 week as follows:

Example 3A - Initial: pH 4.71; 5.35% H2O2; 0.87% PAA. Final: 5.95% H2O2; 0.68% PAA.

Example 3B - Initial: pH 5.05; 4.30% H2O2; 1.14% PAA. Final: 4.83% H2O2; 0.73% PAA.

Example 3C - Initial pH 5.5; 2.92 H2O2; 0.98% PAA. Final: 3.24% H_2O_2; 0.88% PAA.

Example 3D - Initial: pH 5.55; 1.40% H2O2; 0.87% PAA. Final: 1.70% H2O2; 0.81% PAA.

Example 3E - A sample of a gel prepared as above was vacuum dried to a solid which assayed 24.27% H2O2 and 1.08% PAA. After 397 days the sample assayed 17.70% H2O2 and 0.27% PAA.

Example 4

A series of experiments were run to screen various polyacrylate compounds ability to make a thickened aqueous composition containing about 18% by weight hydrogen peroxide (H2O2) and about 3% to 4% peracetic acid (PAA). In each experiment 2% by weight polymer was incorporated into a standard commercial grade of hydrogen peroxide with sodium stannate stabilizer. Sufficient aqueous hydrogen peroxide and sufficient alkali (sodium hydroxide) were added to attempt to adjust the final pH to about 5 to 6. A solution of 5% by weight peracetic acid was then added. In three runs, the polyacrylate was premoistened with isopropanol. The results are presented as Table I. From the table it is clear that a gel or thickened solution could be formed by the process with any cross-linked polyacrylate that increases the viscosity of an aqueous solution.

Table I
Screening Test of Cross-linked Polyacrylates

Carbopol Polymer	H2O2 Gel	% H_2O_2	% PAA	Comments
941	light	17.75	3.80	2 phases after 24 hr
940	thicker	18.16	2.84	bubbles in 24 hr
934	bubbly	17.91	3.45	
934*	foamy	16.93	2.30	*boric acid added
675	slow-forming	18.21	3.48	
613	v.light	18.32	3.77	
675	v.light	18.16	2.98	isopropanol moistened
934	v.light	17.78	3.63	isopropanol moistened
1610	v.light	16.93	2.30	isopropanol moistened

Example 5

Another series of examples were run using Carbopol 934 and hydrogen peroxide contining sodium stannate stabilizer. Hydrogen peroxide and 15% by weight PAA were added in amounts to form a sol of about 34% hydrogen peroxide and 8% to 10% PAA. With 6% polyacrylate a very thick (excellent) gel was formed which remained excellent after 24 hours. With 1.5% polyacrylate a thin sol was formed.

Example 6

A series of examples were run in which standard commercial hydrogen peroxide without sodium stannate and 35% by weight PAA were employed to formulate compositions containing about 1% (or 2%) by weight

peracetic acid. Sols prepared with 1% by weight Carbopol 614, 934, 615 and 617 were not very thick, as expected. Sols containing 1.5% Carbopol 615 and 2% 617 or 614 containing about 2% PAA were very thick.

These examples show that almost any cross-linked polyacrylate polymer can be employed to thicken an aqueous peracetic acid solution by varying the amount of polyacrylate used. Any hydrogen peroxide may be used with or without sodium stannate stabilizer. The ratio of hydrogen peroxide to peracetic acid may also be varied to suit any particular use.

Claims:

1. An aqueous colloidal peroxygen composition characterized by stable sols, gels and solids of C2 to C6 peroxycarboxylic acids and a cross-linked polyacrylate which can retain at least 50% of its total active oxygen for 24 hours when adjusted to a pH of 3 or higher.

2. The composition of claim 1 characterized in that the pH is adjusted between 3 and 10.

3. The composition of claim 1 characterized in that the composition is a viscous sol.

4. The composition of claim 1 characterized in that the composition is a gel.

5. The composition of claim 1 characterized in that the composition is sufficiently dehydrated to be a solid.

6. The composition of claim 2 characterized in that the pH is adjusted between 7 and 10.

7. The composition of claim 2 characterized in that the pH is adjusted to between 8 and 9.5.

8. The process of forming a stable aqueous peroxy-carboxylate gel by incorporating a compound selected from the group consisting of konjac gum, locust bean gum, cross-linked polyacrylate and combinations thereof into an aqueous solution to form an aqueous sol and incorporating therein a peroxycarboxylic acid.

9. The process of claim 8 characterized in that the aqueous solution is water.

10. The process of claim 8 characterized in that the aqueous solution contains hydrogen peroxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/12427

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C01B 15/055
US CL : 252/186.26, 186.23, 186.42
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/186.26, 186.23, 186.42, 186.22, 186.28, 186.29, 186.43

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS text search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US, A, 5,296,239 (COLERY ET AL.) 22 March 1994, see abstract, and column 3, line 34 to column 4, line 45, and examples 1-5.	1, 3-4 --------- 2, 5-10
Y	US, A, 5,160,655 (DONKER ET AL.) 03 November 1992, see abstract, and column 5, line 57 to column 6, line 27.	2, 6-7
Y	US, A, 3,563,687 (MOYER) 16 February 1971, see abstract and column 1, lines 30-58.	2, 6-7
Y	US, A, 5,091,106 (JACOBS ET AL.) 25 February 1992, see abstract, and claims.	5
Y	US, A, 4,879,057 (DANKOWSKI ET AL.) 07 November 1989, see abstract, and column 6, lines 38-54.	8-10

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/12427

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,017,411 (DIEHL ET AL.) 12 April 1977, see abstract, column 4, lines 26-68, and claims.	1-10